

# PATENT SPECIFICATION

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## DRAWINGS ATTACHED

- (21) Application No. 57719/69 (22) Filed 25 Nov. 1969  
 (31) Convention Application No. 175 377 (32) Filed 26 Nov. 1968 in  
 (33) France (FR)  
 (45) Complete Specification published 19 July 1972  
 (51) International Classification C08G 17/01  
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     B1B 3B3  
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 (72) Inventors JACQUES CHARLES, MAURICE LEGER and  
                 LUCIEN MANJOT



## (54) PROCESS FOR THE PREPARATION OF POLYESTERS

(71) We, SOCIETE RHODIACETA, a French Body Corporate of 21 Rue Jean-Goujon, Paris 8e, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly

sively lower pressures and at sufficiently high temperatures to cause the polycondensation of the monomer and the evolution of the volatile by-products, the condensation product and the volatile products passing together from zone to zone in the form of a mixture, in such a way that violent agitation occurs.

This process makes it possible to obtain an homogeneous product, but since the glycol used by the reaction travels in the same direction as the reaction product, the latter is

By a direction given under Section 17 (1) of the Patents Act 1949 this application proceeded in the name of RHONE-POULENC-TEXTILE, a French Body Corporate of 21, Rue Jean-Goujon, Paris 8e, France.

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usually called prepolymer. In the first stage, called precondensation, the monomer is converted into a prepolymer of low molecular weight, which in the second stage, called finishing, is converted into a polyester of high molecular weight.

In order to obtain products of high molecular weight which can be converted into yarns and fibres of high-grade properties it is necessary that the formation of by-products during the precondensation should be limited to the maximum possible extent. In order to do this it is desirable that the necessary heating of the reaction mixture be carried out under such conditions that the gaseous products evolved in the reaction are removed as rapidly as possible, and that the dwell times of the various parts of the reaction mixture should be as uniform as possible.

Hitherto several processes have been conceived for carrying out the precondensation continuously.

In one known technique, the monomer passes through a series of zones at progres-

sive from of glycols which contaminate the product and which are harmful to the properties of high molecular weight polyesters made from the precondensate.

In the process described in U.S. Patent No. 3,192,184 the precondensation is carried out by causing the monomer to flow by gravity down a heated essentially vertical surface comprising protuberances which promote the distribution of the product in the form of a film over the entire area of the surface, the volatile products evolved being removed in counter-current. In this process speed gradients are established across the thickness of the film of reaction mixture when the viscosity of the product becomes significant, so that the material in contact with the treated surface is subjected to the action of heat for a longer time, and hence, undergoes a more extensive change

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(54) PROCESS FOR THE PREPARATION OF  
POLYESTERS

(71) We, SOCIETE RHODIACETA, a French Body Corporate of 21 Rue Jean-Goujon, Paris 8e, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the continuous production of polyesters of low molecular weight from  $\omega$ -hydroxyalkyl esters of dicarboxylic acids, and more particularly to a process and apparatus for the continuous production of prepolymers from bis- $\beta$ -hydroxyethyl terephthalate and/or oligomers thereof.

The continuous production of saturated polyesters from bis- $\omega$ -hydroxyalkyl terephthalates or their oligomers is generally carried out in two stages; during the first stage, usually called prepolymerisation or precondensation, the monomer is converted into a prepolymer of low molecular weight, which in the second stage, called finishing, is converted into a polyester of high molecular weight.

In order to obtain products of high molecular weight which can be converted into yarns and fibres of high-grade properties it is necessary that the formation of by-products during the precondensation should be limited to the maximum possible extent. In order to do this it is desirable that the necessary heating of the reaction mixture be carried out under such conditions that the gaseous products evolved in the reaction are removed as rapidly as possible, and that the dwell times of the various parts of the reaction mixture should be as uniform as possible.

Hitherto several processes have been conceived for carrying out the precondensation continuously.

In one known technique, the monomer passes through a series of zones at progres-

sively lower pressures and at sufficiently high temperatures to cause the polycondensation of the monomer and the evolution of the volatile by-products, the condensation product and the volatile products passing together from zone to zone in the form of a mixture, in such a way that violent agitation occurs.

This process makes it possible to obtain an homogeneous product, but since the glycol liberated by the reaction travels in the same direction as the desired product, the latter is, in its most advanced stage, in contact with a considerable amount of glycol which causes reversal of the reaction regardless of whether the flow occurs horizontally or upwardly as in the process described in U.S. Patent No. 2,727,882, or downwardly as in the process described in French Patent No. 1,198,446.

Furthermore, in the last zones, through which all the glycol vapour liberated during the reaction passes, the temperature and pressure conditions favour the formation therefrom of glycol ethers (e.g. polyethylene glycols) which contaminate the precondensate, and which are harmful to the properties of the high molecular weight polyesters made from the precondensate.

In the process described in U.S. Patent No. 3,192,184 the precondensation is carried out by causing the monomer to flow by gravity down a heated essentially vertical surface comprising protuberances which promote the distribution of the product in the form of a film over the entire area of the surface, the volatile products evolved being removed in counter-current. In this process speed gradients are established across the thickness of the film of reaction mixture when the viscosity of the product becomes significant, so that the material in contact with the treated surface is subjected to the action of heat for a longer time, and hence, undergoes a more extensive change

than that which is spaced from it, with the result that the prepolymer obtained is very heterogeneous.

5 The present invention provides a process for the continuous production of polyesters of low molecular weight, by means of which substantially homogeneous products containing a very low proportion of glycol ethers can be obtained.

10 This process consists in passing a liquid composition comprising an bis- $\omega$ -hydroxyalkyl ester of a dicarboxylic acid, especially terephthalic acid, and/or oligomers thereof into the first of a succession of superposed zones kept at the same pressure below 15 mm Hg and at a temperature above 260°C., in each of which zones the mixture travels in the form of one or more streams which are constrained to come into contact alternately two or more times with a heated wall and with the atmosphere under reduced pressure, the mixture passing downwardly from one zone to the next by gravity in the form of a film, and the gaseous products liberated travelling upwardly through the zones without a pressure drop.

20 The process is of particular value in the production of polyethylene terephthalate from  $\beta$ -hydroxyethyl terephthalate and/or its oligomers, and will be more particularly described by reference to these compounds. It will be understood however that is what is said applies also *mutatis mutandis* to the polymerisation of other  $\omega$ -hydroxyalkyl esters of dicarboxylic acids, especially terephthalic acid.

30 The bis- $\beta$ -hydroxyethyl terephthalate and/or oligomers thereof can be obtained by known techniques, for example by an ester interchange between dimethyl terephthalate and glycol, or by the direct esterification of terephthalic acid with glycol or ethylene oxide.

40 Preferably, the mixture to be treated consists of a mixture of bis- $\beta$ -hydroxyethyl terephthalate and oligomers thereof.

45 Such a mixture can also contain a certain proportion of free ethylene glycol and, in small amounts, diethyl terephthalate and/or the mixed ethyl hydroxyethyl terephthalate.

50 The process is particularly suitable for treating such a mixture in which the molar ratio of free glycol to total glycol is less than 0.05:1 and the molar ratio of total glycol to terephthalate units is between 1.15:1 and 1.50:1.

55 (Total glycol is to be understood as the number of mols of glycol in the free form and in the combined form).

60 Where a mixture is available which results from an ester interchange reaction between a dialkyl terephthalate and glycol or from the direct esterification of terephthalic acid by glycol, in which the molar ratio free glycol to total glycol is greater than 0.1:1, it is preferable to subject this mixture, before subjecting it to the process of the invention, to such tem-

perature and pressure conditions that this ratio is brought to about 0.05:1 or below.

65 The process is particularly useful for the conversion a composition comprising bis- $\beta$ -hydroxyethyl terephthalate and/or oligomers thereof of relative viscosity less than 2, and preferably between 1.20 and 1.60, into a prepolymer of relative viscosity above 2. (The relative viscosity (R.V.) is the ratio of the viscosity at 25°C. of a solution containing 5 g. of solute in 100 ml. of *ortho*-chlorophenol to the viscosity of the pure solvent).

70 The reaction can be carried out by heating the reaction mixture at between 260°C. and 350°C. and preferably between 270° and 290°C. under a pressure less than 15 mm Hg. and preferably between 4 and 10 mm Hg.

75 The temperature and pressure conditions in the process are preferably chosen within the ranges indicated above, to give a prepolymer of R.V. not exceeding 3. At higher RV's viscosity becomes such that the travel of the reaction mixture through the zones is difficult, as is its flow in the form of a thin film.

80 The invention also provides an apparatus for the continuous preparation of a prepolymer by the above process.

85 This apparatus consists of a plurality, preferably 5 or more, of superposed zones, preferably arranged in a column, each having an essentially horizontal base, means for heating each such horizontal base, each zone being vertically divided over part of its height by vertical partitions, so as to form compartments between which are means of communication located alternately at the top and at the bottom of the partitions, the compartments and their means of communication defining a flow path or flow paths in parallel across the zone, and, as the sole means of transfer between any two superposed zones, at least one essentially vertical tube whose lower orifice is above a compartment in the lower of the two zones and at a higher level than that of the highest means of communication of this zone, and which extends into the higher of the two zones between two of the partitions therein, having its upper orifice at a lower level than or approximately the same level as the highest means of communication in its zone, alternate tubes occupying substantially opposite positions across the apparatus, means for keeping all the zones at a particular elevated temperature above 260°C. and a particular sub-atmospheric pressure below 15 mm Hg, and means for feeding liquid to and removing vapour from the highest zone and liquid from the lowest zone. Preferably each zone is divided into at least 4 compartments if there is only one flow path, or into at least 6 compartments if there are two flow paths in parallel.

120 The upper orifice of the transfer tube from one zone to the next can be at a lower level than that of the highest means of communica-

tion in the upper zone, but in a preferred form of the invention it is located at the same, or a slightly higher level. Obviously it must not be high enough to allow the flow path to be short-circuited.

5 The means of communication between the compartments can be of various forms such as slits, channels, and perforations in the partitions. Alternatively the upper means of communication may be provided by making these partitions lower than the others over part or the whole of their widths, so that the reaction mixture flows over the top thereof. Likewise a lower communicating means may be bounded on one side by the base of the zone, again over part or the whole of the width of the partition.

Forms of device according to the invention are described below by reference to the accompanying schematic drawings in which:

20 Figure 1 is a vertical cross-section through an apparatus according to the invention, in the form of a column;

25 Figure 2 is a cross-section of the column at the level A A';

Figure 3 is a perspective view, partly broken away, of one of the reaction zones of the column;

30 Figure 4 is a vertical cross-section through a different type of column; and

Figure 5 is a cross-section of the column of Figure 4 at the level A A'.

Referring now to the drawings the column of Figure 1 comprises a feed tube 1 at the level of the highest zone and a discharge tube 2 below the lowest zone. At the top of the column, a tube 3, equipped with a filter, connects the device to an apparatus used to produce a vacuum in the column and also to a condenser for the vaporous by-products liberated by the reaction. Each zone is provided with a jacket 4 which allows the base and the wall of the zone to be heated by circulation of a hot fluid.

45 The column shown comprises six reaction zones but this number can be higher or lower; the optimum depends essentially on the flow rate of the starting composition the characteristics of the prepolymer to be obtained, and the length of the flow path provided for the reaction mixture across the zones. However, the number is preferably not less than 5.

50 Each zone communicates with the next by means of a transfer tube 5, down whose inner wall the reaction mixture can flow as a thin film.

60 As shown in Figures 2 and 3, each zone is divided, over part of its height, into six compartments in the form of sectors by means of radial baffles, baffles 6A extending to a higher level than the others 6B. The higher baffles

6A have a cut away portion 7 at their lower edge, which provides a means of communication between the two compartments separated by the baffle. The means of communication between the other pairs of compartments is provided by the lower level of the upper edge 8 of the corresponding baffles, which allows the reaction mixture to flow over the top of these baffles. Thus the baffles taken as a whole force the reaction mixture to flow through each zone in two flow paths in parallel (indicated by the arrows) which alternate between contact with the heated base of the zone and direct exposure to the reduced atmospheric pressure which is maintained in the column. The upper opening of the transfer tube 5 is at a level between those of the tops of the higher and lower baffles 6A, 6B respectively, so that in entering it the reaction mixture is exposed a second time to the reduced atmospheric pressure.

Although the number of compartments shown is 6, it may be more or less than this, provided the mixture comes into contact with the heated base and with the atmosphere under reduced pressure more than once during its travel through each zone.

The transfer tubes 5 are staggered from one zone to the next so as to be located at the ends of the flow paths defined in each zone.

The column shown in Figures 4 and 5 is similar to that described above except that the compartments are separated by parallel baffles 6, of differing heights, and the transfer tubes 5 open at a level below the upper edge of the higher of the baffles 6. The transfer tubes are formed by the final baffle and the wall of the column.

In Figures 1 and 4 the full arrows indicate the flow of liquid, and the broken arrows the flow of vapour, from one zone to the next.

The following Examples illustrate the invention.

#### EXAMPLES 1, 2, 3 AND 4

A column of the type shown in Figure 1 comprises 6 reaction zones of diameter 150 mm and 150 mm high connected by transfer tubes of diameter 50 mm. Each zone comprises 6 radial partitions in the form of baffles, as shown in Figures 2 and 3, the upper level of each transfer tube being located 60 mm above the bottom of the corresponding zone.

This column is fed with a mixture of bis- $\beta$ -hydroxyethyl terephthalate and its oligomers, containing 338 parts by weight per million parts of ethylene terephthalate units of antimony oxide; the characteristics of the mixture are given in the Table below, which also shows the operating conditions and the results obtained.

Feed mixture			Feed rate kg/h.	Conditions in the column		Prepolymer obtained		$\Delta$ Proportion of ether
R.V.	Ratio Total glycol/terephthal- ate units	Ratio free glycol/ total glycol		Temper- ature	Pressure *	RV.	Ratio total glycol/ terephthalate units	
1.48	1.31	0.019	10.22	280°C	7	2.52	1.06	0.39
1.47	1.37	0.027	11.4	270°C	4	2.06	1.06	0.32
1.46	1.48	0.021	7.78	280°C	7	2.48	1.07	0.69
1.45	1.38	0.025	11.3	275°C	10	2.07	1.05	0.37

\* in mm Hg

The prepolymers obtained under these conditions have a significantly narrower molecular weight distribution than those obtained by processes in which the dwell time is less well controlled.

The  $\Delta$  proportion of ether expresses the difference between the percentage of ether groups in the feed mixture and that in the prepolymer obtained. The percentage of ether groups here denotes the percentage by weight of aliphatic ether bonds, expressed as diethylene glycol, in the polymer chain. The concentration of ether groups can be easily determined by known chemical methods and by infrared absorption spectra.

#### EXAMPLE 5

In this Example a column of the same type as that employed in Example 1 but comprising 8 reaction zones 180 mm high of diameter 250 mm connected by transfer tubes of diameter 80 mm is used. Each zone comprises 6 radial partitions arranged as baffles, and the height of the transfer tube above the base of each zone is 82.5 mm.

A mixture of bis- $\beta$ -hydroxyethyl terephthalate and its oligomers, of relative viscosity 1.42, in which the ratio total glycol/terephthalate units is 1.49 and the ratio free glycol/total glycol is 0.039, and which contains 170 parts per million of antimony oxide (on the same basis as before), is introduced at a flow rate of 52 kg/hour into the column, which is kept at 280°C. and under a pressure of 7 mm Hg.

A prepolymer of relative viscosity 2.17, in which the ratio total glycol/terephthalate units is 1.14, is obtained.

The  $\Delta$  proportion of ether is 0.30.

#### WHAT WE CLAIM IS:—

1. Process for continuously obtaining polyesters of low molecular weight from a liquid composition consisting essentially of a bis-hydroxyalkyl ester of a dicarboxylic acid and/or oligomers thereof, which comprises passing the composition through a succession of superposed zones kept at the same pressure below 15 mm Hg, and at a temperature above 260°C., in each of which the mixture travels

- in the form of one or more streams which are constrained to come into contact alternately two or more times with a heated wall and with the atmosphere under reduced pressure, the mixture passing downwardly from one zone to the next by gravity in the form of a film, and the gaseous products liberated travelling upwardly through the zones without a pressure drop.
2. Process according to claim 1, in which the ester is bis- $\beta$ -hydroxyethyl terephthalate.
3. Process according to claim 2, in which the liquid composition is a mixture of bis- $\beta$ -hydroxyethyl terephthalate and oligomers thereof.
4. Process according to claim 3, in which the mixture has a relative viscosity below 2, a molar ratio of free glycol to total glycol less than 0.05, and a molar ratio of total glycol to terephthalate units between 1.15 and 1.50.
5. A process according to claim 1 substantially as herein before described.
6. Apparatus suitable for use in the process of claim 1, comprising a plurality of superposed zones each having an essentially horizontal base, means for heating each such horizontal base, each zone being vertically divided, over part of its height, by vertical partitions so as to form compartments between which are means of communication located alternately at the top and at the bottom of the partitions, the compartments and their means of communication defining a flow path or flow paths in parallel across the zone, and, as the sole means of transfer between any two superposed zones, at least one essentially vertical tube whose lower orifice is above a compartment in the lower of the two zones and at a higher level than that of the highest means of communication of this zone, and which extends into the higher of the two zones between two of the partitions therein, having its upper orifice at a lower level than or approximately the same level as the highest means of communication in its zone, alternate tubes occupying substantially opposite positions across the apparatus, means for keeping all the zones at a particular elevated temperature above 260°C. and a particular sub-atmospheric pressure below 15 mm Hg, and means for feeding liquid to and removing vapour from the highest zone and removing liquid from the lowest zone.
7. Apparatus according to claim 6, comprising a column divided by horizontal partitions into a plurality of superimposed zones, the said horizontal partitions being provided with heating means, each zone being divided into a plurality of compartments by vertical partitions, and the substantially vertical tubes passing through the horizontal partitions.
8. Apparatus according to claim 7, wherein the vertical partitions are radially arranged.
9. Apparatus according to claim 7, wherein the vertical partitions are parallel.
10. Apparatus according to any one of claims 6—9 comprising at least 5 superimposed zones each divided into at least 4 compartments, or into at least 6 compartments if there are two parallel flow paths.
11. Apparatus according to claim 6 substantially as described by reference to, or as illustrated in, the accompanying drawings.
12. A process according to any one of claims 1—5 when carried out in apparatus claimed in any one of claims 6—11.
13. Polyethylene terephthalate and other polyalkylene esters of dicarboxylic acids of low molecular weight obtained by a process claimed in any one of claims 1—5 and 12.
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Fig. 1.

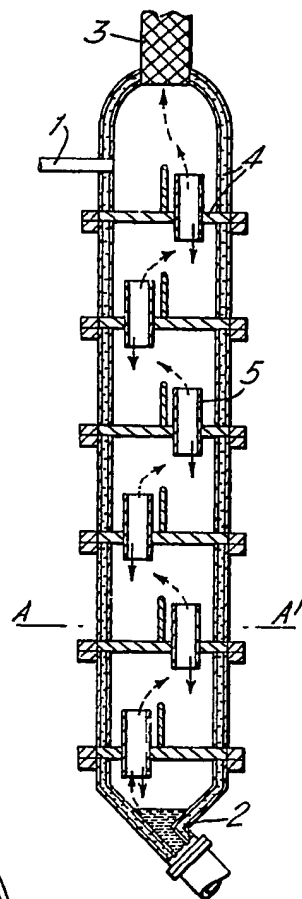


Fig. 2.

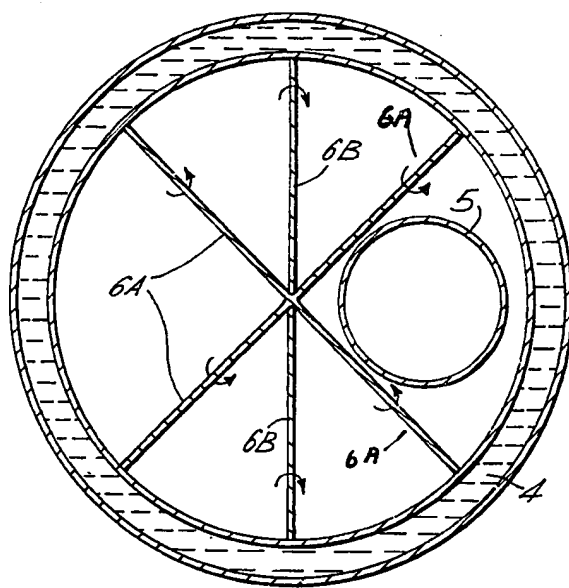
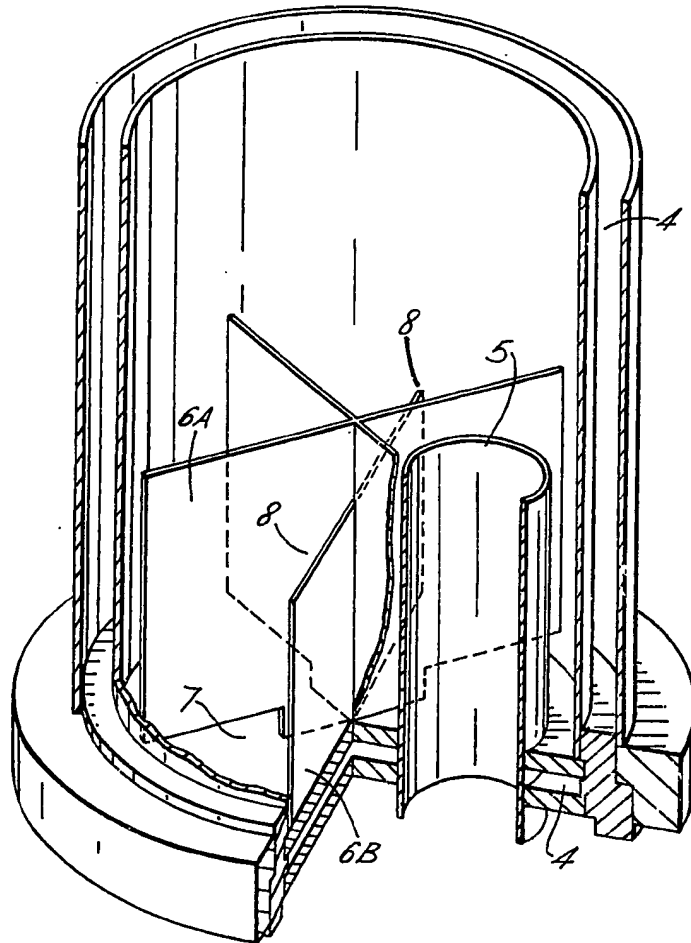


Fig. 3.





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COMPLETE SPECIFICATION

3 SHEETS

This drawing is a reproduction of  
the Original on a reduced scale

Sheet 3

